

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

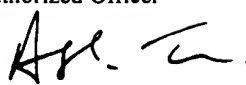
(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference #40210281 DVG:JMD	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).	
International Application No. PCT/AU00/00236	International Filing Date (day/month/year) 23 March 2000	Priority Date (day/month/year) 23 March 1999
International Patent Classification (IPC) or national classification and IPC Int. Cl. ⁷ C08K 3/04; C04B 35/52, 35/524		
Applicant THE UNIVERSITY OF MELBOURNE et al		

1.	This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.																
2.	This REPORT consists of a total of 5 sheets, including this cover sheet. <input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of 10 sheet(s).																
3.	This report contains indications relating to the following items: <table border="0"> <tr> <td>I</td> <td><input checked="" type="checkbox"/> Basis of the report</td> </tr> <tr> <td>II</td> <td><input type="checkbox"/> Priority</td> </tr> <tr> <td>III</td> <td><input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td>IV</td> <td><input type="checkbox"/> Lack of unity of invention</td> </tr> <tr> <td>V</td> <td><input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td>VI</td> <td><input checked="" type="checkbox"/> Certain documents cited</td> </tr> <tr> <td>VII</td> <td><input type="checkbox"/> Certain defects in the international application</td> </tr> <tr> <td>VIII</td> <td><input checked="" type="checkbox"/> Certain observations on the international application</td> </tr> </table>	I	<input checked="" type="checkbox"/> Basis of the report	II	<input type="checkbox"/> Priority	III	<input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability	IV	<input type="checkbox"/> Lack of unity of invention	V	<input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement	VI	<input checked="" type="checkbox"/> Certain documents cited	VII	<input type="checkbox"/> Certain defects in the international application	VIII	<input checked="" type="checkbox"/> Certain observations on the international application
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Date of submission of the demand 2 October 2000	Date of completion of the report 7 August 2001
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer  DR. A. TESSEMA Telephone No. (02) 6283 2271

I. Basis of the report

1. With regard to the elements of the international application:*
- ☐ the international application as originally filed.
- ☒ the description, pages 5, 7, 8, 10-13, as originally filed,
pages 1-4, 9, received on 8 June 2001 with the letter of 8 June 2001,
pages 6, received on 19 February 2001 with the letter of 19 February 2001
- ☒ the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages 14-17, received on 8 June 2001 with the letter of 8 June 2001
- ☒ the drawings, pages 1/6-6/6, as originally filed,
pages , filed with the demand,
pages , received on with the letter of
- ☐ the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , received on with the letter of
2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language which is:
- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).
3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
4. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig.
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Claims 1-32	YES
	Claims 33-39	NO
Inventive step (IS)	Claims 1-27	YES
	Claims 28-32, 33-39	NO
Industrial applicability (IA)	Claims 1-39	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)**NOVELTY; INVENTIVE STEP: Claims 28 - 32 and 33 - 39**

(a) EP 818510 (b) JP 4-117439 (c) JP 9-132461 (d) JP 7-315931 (e) US 4983451
 (f) JP 3-187908 (g) EP 466962

The invention defined in claims 33 - 39 is fully disclosed by each of documents (a) and (b). Each document discloses a composition comprising mesophase carbon/mesocarbon, a phenolic resin and an inorganic filler such as silicone carbide[see col. 1, line 23-col. 2, line 53, col. 3, line 14-col. 4, line 13, claims 1-6, 8 and 9 of (a) and abstract of (b)]. A method of producing the composition as well as an article manufactured from the composition is also disclosed by each of documents (a) and (b). Therefore, present claims 33 - 39 do not satisfy the PCT requirements of novelty and inventive step.

The invention defined in claims 28 - 32, and 33 - 39 does not involve an inventive step in the light of each of documents (c) to (g) and (a) and (b) (see novelty objection above), respectively. Each document discloses a composition comprising mesophase carbon/mesocarbon and a phenolic resin [see abstracts of (c), (d), (f); col. 1, lines 13-15, col. 4, lines 33-59, col. 5, line 63 - col. 6, line 17, claims 1, 2, and 8 of (e); and whole document of (g)]. These documents do not disclose the inorganic filler defined in present claim 28; however, there is no disclosure in the present application which suggests that the inclusion of the inorganic filler in the present composition results in a product superior over that of the prior art. Indeed page 2, line 19, of the present application indicates that the inorganic filler is not essential to the present invention; this is further supported by the absence of such a filler in examples 1 and 2 which are allegedly defining the claimed invention. Furthermore, the feature that allegedly distinguishes the claimed invention from the prior art, that is the synthetic mesophase carbon is " derived from aromatic hydrocarbons ", (see claim 1) is not included in independent claim 28 (see also observation 2 in Box VIII). As there is no suggestion in the description that an unexpected result is achieved by the inclusion of the inorganic filler in the present composition, the invention defined in the above claims cannot be considered to involve an inventive step.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/AU00/00236

VI. Certain documents cited**1. Certain published documents (Rule 70.10)**

Application No. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO 9965843	23 December 1999	21 May 1999	28 May 1998

2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure	Date of non-written disclosure (day/month/year)	Date of written disclosure referring to non- written disclosure (day/month/year)
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VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

1. The scope of claim 21 is unclear because the term " the polymer or polymer composite " does not have antecedent in any one of the preceding claims.

A similar observation applies to claims 23 and 26.

2. The invention defined in claim 28 is not fully supported by the description because it omits the feature that the synthetic mesophase carbon is " derived from aromatic hydrocarbons ". This feature is described at page 2, lines 23-24, as an essential feature of the invention and, hence, independent claim 28 is required to define this feature (see also inventive step objection in Box V).

3. The term " presented " in claim 21 should be " present ".

IMPROVED CARBON-CONTAINING MATERIALS

The invention relates to improved carbon-containing materials, methods for their preparation and articles manufactured from them, in particular steel fabrication equipment, electrodes in electrolytic cells used in aluminium production, refractories in high temperature furnaces and other engineering products.

Carbon bonded composite materials are finding increasing use as replacements for traditional ceramic composites. Such replacement usually results in greatly improved properties and processing ability. Examples can be found in a wide range of industries which include those manufacturing refractory products such as steel fabrication equipment and electrolytic cells used in aluminium production.

In the preparation of carbon bonded composites, an organic polymer phase is converted to a type of carbon during heating which usually progresses through various temperatures of up to 2000°C. These composites also generally contain carbon black fillers which are added to control rheological properties, assist in processing or improve mechanical properties. The physical state of the carbon may vary from fine particles to fibers and platelets.

Although this practice has been adopted for many years, the effect of carbon black on the organic polymer phase formation during curing and the carbon structure produced during pyrolysis has received little or no attention. We have now found that carbon black has a significant impact on the final formation of the carbon material from the polymer. In general, the porosity of the carbon material derived from polymer resin will increase when more carbon black is added. This porous structure results in low density and sub optimum mechanical properties. We have also found that other carbon sources such as pulverized graphite or carbon derived from pyrolysis of phenolic resins exhibit similar effects to carbon black.

Mesophase carbon was developed in the last few years for the purpose of making graphitic carbon at relative low temperatures of 2000 to 2500°C. Mesophase carbon may be derived synthetically from aromatic hydrocarbons or

from petroleum pitch. Synthetic mesophase which can be derived from aromatic hydrocarbons such as naphthalene consists of up to 100% anisotropy, while mesophase derived from petroleum pitch usually has only up to 75% anisotropy. Synthetic mesophase was developed as a superior precursor to graphitisation and
5 is extensively used in carbon fiber applications. Such materials are usually used as a binderless mould and application temperatures are generally more than 2000°C.

We have now found that when synthetic mesophase carbon derived from aromatic hydrocarbons is used as a filler in combination with an organic polymer binder that carbon materials having unexpected and improved properties are
10 obtained. These carbon materials generally have a low porosity measured as a low surface area, high carbon yield, high composite density and good mechanical properties.

According to one aspect of the present invention there is provided a composition suitable for the preparation of a carbon-containing material including:

- 15 (i) a binder phase containing an organic resin component or a polymer composite;
(ii) synthetic mesophase carbon derived from aromatic hydrocarbons;
and
(iii) optionally filler particles.

20 According to another aspect of the present invention there is provided a method for preparing a carbon-containing material including the steps of:

- (a) mixing a binder phase containing an organic resin component or polymer composite with synthetic mesophase carbon derived from aromatic hydrocarbons and optionally filler particles;
25 (b) curing the mixture; and
(c) heating the cured mixture.

The term "organic resin component" is used herein in its broadest sense to denote low molecular weight polymerisable entities through to higher molecular weight entities containing many repeat units. The term includes monomers,
30 dimers and oligomers.

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A wide range of resin structures are possible but generally this structure will be dictated by resins with a low number of heteroatoms and high carbon content. Suitable resins are those of the formulae (I) and (II) respectively:



wherein X is oxygen, sulphur or nitrogen and R is aryl, imidoaryl, alkyl, alkenyl, alkynyl or heterocyclyl which may be optionally substituted.

In this specification "optionally substituted" means a group that may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, alkynyloxy, aryloxy, carboxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloalkynyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, azido, amino, alkylamino, alkenylamino, alkynylamino, arylamino, benzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, acyloxy, aldehydo, alkylsulphonyl, arylsulphonyl, alkylsulphonylamino, arylsulphonylamino, alkylsulphonyloxy, arylsulphonyloxy, heterocyclyl, heterocycloxy, heterocyclylamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, arylthio, acylthio and the like.

Organic resins components having hydroxyl groups such as those of the formulae (I) and (II) above wherein X is oxygen and R is optionally substituted aryl, for example, phenolic resins or substituted phenolic resins are preferred. Suitable phenolic resins include phenol-aldehyde type resins such as phenol-formaldehyde type resins, for example, resole or novolac and phenolic imide or phenolic polyimide. It will be appreciated that the phenolic resins may be substituted with any non-deleterious substituent including alkyl, for example, methyl or t-butyl; or imide, for example, maleimide or succinimide.

The desirable composite will have a heteroatom, such as nitrogen in the system from polymer or crosslinker or solvent. This can be done by using an organic binder having nitrogen, such as polyimide; crosslinker, such as HMTA; or a solvent, such as pyridine.

The term "polymer composite" is used herein in its broadest sense and refers to the combination of an organic resin component with another material, such as, for example, other polymers, particulate matter and/or additives known in the polymer art. It will be appreciated that one or more of the other materials may be inert or chemically reactive. The polymers may be selected from those defined above and can be in the form of a solution, dispersions, fibers or particles. The additives may include crosslinkers such as hexamine which is also known as hexamethylene tetramine (HMTA), polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and sources of formaldehyde such as formalin, paraform or trioxane. Suitable polymer composites include novolac-HMTA, novolac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resole-carbon-novolac-HMTA-FA, novolac-HMTA-FA-carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂-resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA and polyimide-novolac. A preferred polymer composite is novolac-FA-HMTA.

The mesophase carbon can be in the form of fibers, pellets, platelets or powder. The powder form can be obtained by pulverising the mesophase in a ball mill. As discussed above, the mesophase may be derived synthetically from aromatic hydrocarbons such as naphthalene. Examples include 100% anisotropic mesophase derived from naphthalene. The 100% anisotropic naphthalene may be prepared by cationic oligomerisation catalysed by HF/BF₃. The mesophase may be untreated or pre-treated by heating generally up to about 600°C.

The selection of filler particles largely depends upon the intended use of the carbon containing material. Examples of particulate matter include coated or uncoated fibers, platelets, pigments, fillers, polyesters, metallic mesh, silicon oxides, graphite, carbon black, carbides or nitrides and inorganic material such as aluminium, magnesia, zirconia, bauxite, clay, alumina, titanium diboride, zirconium diboride or titanium oxide. For instance, the inclusion of titanium diboride fillers provides a carbon material which can be used as a wetted cathode in advanced aluminium reduction cells.

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The carbon-containing material of the present invention has many desirable properties including controlled surface area, high density, good mechanical strength, Strain to Failure (StF) values and anti-corrosion properties. For example, the carbon-containing material may have a total surface area of 20 m²/g (Langmuir method) which gives excellent anti-corrosion, a high mechanical strength of about 60 MPa after curing and about 58 MPa after heating, a high carbon density of more than about 1.4 g/cm³ and improved oxidation resistance with the oxidation temperature under O₂ being higher than about 570°C.

These desirable properties enable the carbon-containing material of the present invention to have various industrial applications. High performance carbon materials having anti-corrosion properties are often required by the refractory industry to form cathodes in aluminium reduction cells or bricks in steel making vessels. On the other hand, good mechanical and anti-oxidation properties of carbon materials are important in the products used in steel processing.

Thus, the present invention also extends to articles manufactured from the carbon-containing material, made from ferrous and non ferrous materials, glasses and ceramics, for example, steel fabrication equipment such as slide gates or valves, tap hole blockers and blast furnace linings, electrolytic cells used in aluminium production and other engineering products such as thermal protection barriers, aerospace components and aircraft, satellite and space craft structures.

The method used to prepare the carbon-containing material of the present invention is simple and the precursors of the binder phase and the mesophase carbon are commercially available and cheap. Accordingly, the present invention has the capability of producing a high performance material in an efficient and economical way.

The invention will now be described with reference to the following examples. These examples are not to be construed as limiting the invention in any way.

In the examples, reference will be made to the accompanying drawings in which:

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other carbon sources. These carbon sources include pulverised graphite, carbon obtained from the pyrolysis of pure novolac/HMTA/FA to 1000°C and carbon of the same pure resin after pre-treatment using the profile described in Example 1. The resulting mixtures were then cured and pyrolysed to 1000°C as described in Example 1. Table 1 shows that these carbon sources have similar effects to carbon black on the porosity of the final formed carbon/carbon composite.

Different types of mesophase were tested under the same conditions and the results are shown in Table 1 below. The other mesophase carbon used was mesophase derived from naphthalene without pre-treatment. Table 1 indicates that this mesophase carbon has a similar effect on the porosity of the final formed carbon materials as the pre-treated mesophase. The pyrolysis weight loss is also much higher.

Table 1. Effect of other carbon fillers on the carbon material formation from a novolac/HMTA/FA mixed system

	50% Carbon Black	50% pre-treated mesophase	50% graphite	50% resin carbon	50% pre- treated resin	50% un-treated mesophase
Cure Weight Loss (%)	11	12	10	19	12	11
Pyrolysis Weight Loss (%)	18	25	19	25	21	35
Surface Area (m ² /g)	266	33	46	266	215	12

Claims

1. A composition suitable for the preparation of a carbon-containing material including:
 - 5 (i) a binder phase including an optionally substituted phenolic resin;
 - (ii) synthetic mesophase carbon from aromatic hydrocarbons and;
 - (iii) inorganic filler particles suitable for use as refractory material for high temperature applications.
2. A composition is claimed in claim 1 wherein the phenolic resin is a phenol-
10 aldehyde type resin.
3. A composition is claimed in claim 2 wherein the phenol-aldehyde type resin is a phenol-formaldehyde type resin.
4. A composition as claimed in any one of claims 1 to 3 wherein the phenolic resin is selected from either resole or novolac and phenolic imide or phenolic
15 polyamide or mixtures thereof.
5. A composition as claimed in any one of claims 1 to 4 wherein the phenolic resin is substituted with alkyl or imide.
6. A composition as claimed in claim 5 wherein the alkyl is methyl or t-butyl.
7. A composition as claimed in claim 5 wherein the imide is maleimide or
20 succinimide .
8. A composition as claimed in any one of claims 1 to 7 where the refractory material is one or more of non oxide refractory materials.
9. A composition as claimed in claim 8 wherein the non oxide refractory material is boride, carbide and/or nitride.
- 25 10. A composition as claimed in claim 9 wherein the boride is titanium diboride and/or zirconium diboride.
11. A composition as claimed in claim 9 wherein the carbide is silicon carbide or titanium carbide.
12. A composition as claimed in claim 9 wherein the nitride is silicon nitride or
30 aluminium nitride.

13. A composition as claimed in any one of claims 1 to 12 further comprising an additive selected from the group consisting of crosslinkers, polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and/or sources of formaldehyde.
- 5 14. A composition as claimed in claim 13 wherein the crosslinker is hexamine (hexamethylene tetramine (HMTA)).
15. A composition as claimed in claim 13 wherein the source of formaldehyde is formalin, paraform or trioxane.
- 10 16. A composition as defined in any one of claims 1 to 15 wherein the binder phase is selected from the group consisting of novolac-HMTA, novolac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resol-carbon-novolac-HMTA-FA, novolac-HMTA-FA carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂ resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA or polyimide-novolac.
- 15 17. A composition as defined in claim 16 wherein the binder phase is novolac-FA-HMTA.
18. A composition as claimed in any one of claims 1 to 17 wherein the mesophase carbon is in the form of fibres, pellets, platelets or powder.
19. A composition as claimed in any one of claims 1 to 18 wherein the
20 mesophase carbon is 100% anisotropic mesophase derived from naphthalene.
20. A composition as claimed in any one of claims 1 to 18 wherein the mesophase carbon is pre-treated by heating.
21. A composition as claimed in any one of claims 1 to 19 wherein the polymer or polymer composite and/or mesophase carbon are presented in the form of a
25 solution.
22. A composition as claimed in claim 21 wherein the solvent used in the solution is inert or chemically reactive.
23. A composition as claimed in claim 22 wherein the solvent is incorporated in the polymer or polymer composite.
- 30 24. A composition as claimed in claim 22 or claim 23 wherein the solvent is water or an organic solvent.

25. A composition as claimed in claim 24 wherein the organic solvent is an aromatic, ketone, alcohol, ester, ether or mixtures thereof.
26. A composition as claimed in any one of claims 1 to 25 wherein other additives known in the polymer art are included in the polymer, polymer composite
5 and/or synthetic mesophase carbon mixture.
27. A composition as claimed in any one of claims 21 to 26 wherein the mesophase carbon is combined with a solution of novolac/HMTA/FA.
28. A method for preparing a carbon-containing material including the steps of:
 (a) mixing a binder phase containing an organic resin component or
10 polymer composite with synthetic mesophase carbon and inorganic filler particles suitable for use as refractory material for high temperature applications;
 (b) curing the mixture; and
 (c) carbonising the cured mixture to above 800°C.
29. A method as claimed in claim 28 wherein the mixture of the binder phase
15 and the mesophase carbon is cured at temperatures up to about 205°C under pressure.
30. A method as claimed in claim 28 or 29 wherein the cured mixture is heated up to temperatures above about 800°C.
31. A method as claimed in claim 30 wherein the temperature is about 1000°C.
- 20 32. An article which is wholly or partly manufactured from the carbon-containing material defined in any one of claims 1 to 32.
33. An article as claimed in claim 32 which is steel fabrication equipment or other engineering products.
34. An article as claimed in claim 33 wherein the steel fabrication equipment is
25 slide gates or valves, tap hole blockers or blast furnace linings.
35. An article as claimed in claim 34 which is used as part of an electrode in the electrolytic production of metals.
36. An article as claimed in claim 35 wherein the metals are aluminium and/or magnesium.
- 30 37. An article as claimed in claim 32 or 36 which is used as a refractory liner in furnaces used for high temperature processing of materials.

38. An article as claimed in claim 37 wherein the materials are ferrous and non ferrous metals, glasses and ceramics.

39. An article as claimed in claim 33 wherein the engineering product is thermal protection barriers, aerospace components or aircraft, satellite or space craft
5 structures.

The carbon-containing material of the present invention has many desirable properties including controlled surface area, high density, good mechanical strength, Strain to Failure (StF) values and anti-corrosion properties. For example, the carbon-containing material may have a total surface area of 20 m²/g (Langmuir method) which gives excellent anti-corrosion, a high mechanical strength of about 60 MPa after curing and about 58 MPa after heating, a high carbon density of more than about 1.4 g/cm³ and improved oxidation resistance with the oxidation temperature under O₂ being higher than about 570°C.

These desirable properties enable the carbon-containing material of the present invention to have various industrial applications. High performance carbon materials having anti-corrosion properties are often required by the refractory industry to form cathodes in aluminium reduction cells or bricks in steel making vessels. On the other hand, good mechanical and anti-oxidation properties of carbon materials are important in the products used in steel processing.

Thus, the present invention also extends to articles manufactured from the carbon-containing material, made from ferrous and non ferrous materials, glasses and ceramics, for example, steel fabrication equipment such as slide gates or valves, tap hole blockers and blast furnace linings, electrolytic cells used in aluminium production and other engineering products such as thermal protection barriers, aerospace components and aircraft, satellite and space craft structures.

The method used to prepare the carbon-containing material of the present invention is simple and the precursors of the binder phase and the mesophase carbon are commercially available and cheap. Accordingly, the present invention has the capability of producing a high performance material in an efficient and economical way.

The invention will now be described with reference to the following examples. These examples are not to be construed as limiting the invention in any way.

In the examples, reference will be made to the accompanying drawings in which:

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IMPROVED CARBON-CONTAINING MATERIALS

The invention relates to improved carbon-containing materials, methods for their preparation and articles manufactured from them, in particular steel fabrication equipment, electrodes in electrolytic cells used in aluminium production, refractories in high temperature furnaces and other engineering products.

Carbon bonded composite materials are finding increasing use as replacements for traditional ceramic composites. Such replacement usually results in greatly improved properties and processing ability. Examples can be found in a wide range of industries which include those manufacturing refractory products such as steel fabrication equipment and electrolytic cells used in aluminium production.

In the preparation of carbon bonded composites, an organic polymer phase is converted to a type of carbon during heating which usually progresses through various temperatures of up to 2000°C. These composites also generally contain carbon black fillers which are added to control rheological properties, assist in processing or improve mechanical properties. The physical state of the carbon may vary from fine particles to fibers and platelets.

Although this practice has been adopted for many years, the effect of carbon black on the organic polymer phase formation during curing and the carbon structure produced during pyrolysis has received little or no attention. We have now found that carbon black has a significant impact on the final formation of the carbon material from the polymer. In general, the porosity of the carbon material derived from polymer resin will increase when more carbon black is added. This porous structure results in low density and sub optimum mechanical properties. We have also found that other carbon sources such as pulverized graphite or carbon derived from pyrolysis of phenolic resins exhibit similar effects to carbon black.

Mesophase carbon was developed in the last few years for the purpose of making graphitic carbon at relative low temperatures of 2000 to 2500°C. Mesophase carbon may be derived synthetically from aromatic hydrocarbons or

from petroleum pitch. Synthetic mesophase which can be derived from aromatic hydrocarbons such as naphthalene consists of up to 100% anisotropy, while mesophase derived from petroleum pitch usually has only up to 75% anisotropy. Synthetic mesophase was developed as a superior precursor to graphitisation and is extensively used in carbon fiber applications. Such materials are usually used as a binderless mould and application temperatures are generally more than 2000°C.

We have now found that when synthetic mesophase carbon derived from aromatic hydrocarbons is used as a filler in combination with an organic polymer binder that carbon materials having unexpected and improved properties are obtained. These carbon materials generally have a low porosity measured as a low surface area, high carbon yield, high composite density and good mechanical properties.

According to one aspect of the present invention there is provided a composition suitable for the preparation of a carbon-containing material including:

- (i) a binder phase containing an organic resin component or a polymer composite;
- (ii) synthetic mesophase carbon derived from aromatic hydrocarbons; and
- (iii) optionally filler particles.

According to another aspect of the present invention there is provided a method for preparing a carbon-containing material including the steps of:

- (a) mixing a binder phase containing an organic resin component or polymer composite with synthetic mesophase carbon derived from aromatic hydrocarbons and optionally filler particles;
- (b) curing the mixture; and
- (c) heating the cured mixture.

The term "organic resin component" is used herein in its broadest sense to denote low molecular weight polymerisable entities through to higher molecular weight entities containing many repeat units. The term includes monomers, dimers and oligomers.

A wide range of resin structures are possible but generally this structure will be dictated by resins with a low number of heteroatoms and high carbon content. Suitable resins are those of the formulae (I) and (II) respectively:



wherein X is oxygen, sulphur or nitrogen and R is aryl, imidoaryl, alkyl, alkenyl, alkynyl or heterocyclyl which may be optionally substituted.

In this specification "optionally substituted" means a group that may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, alkynyloxy, aryloxy, carboxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloalkynyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, azido, amino, alkylamino, alkenylamino, alkynylamino, arylamino, benzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, acyloxy, aldehydo, alkylsulphonyl, arylsulphonyl, alkylsulphonylamino, arylsulphonylamino, alkylsulphonyloxy, arylsulphonyloxy, heterocyclyl, heterocycloxy, heterocyclylamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, arylthio, acylthio and the like.

Organic resins components having hydroxyl groups such as those of the formulae (I) and (II) above wherein X is oxygen and R is optionally substituted aryl, for example, phenolic resins or substituted phenolic resins are preferred. Suitable phenolic resins include phenol-aldehyde type resins such as phenol-formaldehyde type resins, for example, resole or novolac and phenolic imide or phenolic polyimide. It will be appreciated that the phenolic resins may be substituted with any non-deleterious substituent including alkyl, for example, methyl or t-butyl; or imide, for example, maleimide or succinimide.

The desirable composite will have a heteroatom, such as nitrogen in the system from polymer or crosslinker or solvent. This can be done by using an organic binder having nitrogen, such as polyimide; crosslinker, such as HMTA; or a solvent, such as pyridine.

The term "polymer composite" is used herein in its broadest sense and refers to the combination of an organic resin component with another material, such as, for example, other polymers, particulate matter and/or additives known in the polymer art. It will be appreciated that one or more of the other materials may be inert or chemically reactive. The polymers may be selected from those defined above and can be in the form of a solution, dispersions, fibers or particles. The additives may include crosslinkers such as hexamine which is also known as hexamethylene tetramine (HMTA), polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and sources of formaldehyde such as formalin, paraform or trioxane. Suitable polymer composites include novolac-HMTA, novalac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resole-carbon-novolac-HMTA-FA, novolac-HMTA-FA-carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂-resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA and polyimide-novolac. A preferred polymer composite is novolac-FA-HMTA.

The mesophase carbon can be in the form of fibers, pellets, platelets or powder. The powder form can be obtained by pulverising the mesophase in a ball mill. As discussed above, the mesophase may be derived synthetically from aromatic hydrocarbons such as naphthalene. Examples include 100% anisotropic mesophase derived from naphthalen. The 100% anisotropic naphthalene may be prepared by cationic oligomerisation catalysed by HF/BF₃. The mesophase may be untreated or pre-treated by heating generally up to about 600°C.

The selection of filler particles largely depends upon the intended use of the carbon containing material. Examples of particulate matter include coated or uncoated fibers, platelets, pigments, fillers, polyesters, metallic mesh, silicon oxides, graphite, carbon black, carbides or nitrides and inorganic material such as aluminium, magnesia, zirconia, bauxite, clay, alumina, titanium diboride, zirconium diboride or titanium oxide. For instance, the inclusion of titanium diboride fillers provides a carbon material which can be used as a wetted cathode in advanced aluminium reduction cells.

other carbon sources. These carbon sources include pulverised graphite, carbon obtained from the pyrolysis of pure novolac/HMTA/FA to 1000°C and carbon of the same pure resin after pre-treatment using the profile described in Example 1. The resulting mixtures were then cured and pyrolysed to 1000°C as described in Example 1. Table 1 shows that these carbon sources have similar effects to carbon black on the porosity of the final formed carbon/carbon composite.

Different types of mesophase were tested under the same conditions and the results are shown in Table 1 below. The other mesophase carbon used was mesophase derived from naphthalene without pre-treatment. Table 1 indicates that this mesophase carbon has a similar effect on the porosity of the final formed carbon materials as the pre-treated mesophase. The pyrolysis weight loss is also much higher.

Table 1. Effect of other carbon fillers on the carbon material formation from a novolac/HMTA/FA mixed system

	50% Carbon Black	50% pre-treated mesophase	50% graphite	50% resin carbon	50% pre- treated resin	50% un-treated mesophase
Cure Weight Loss (%)	11	12	10	19	12	11
Pyrolysis Weight Loss (%)	18	25	19	25	21	35
Surface Area (m ² /g)	266	33	46	266	215	12

Claims

1. A composition suitable for the preparation of a carbon-containing material including:
 - 5 (i) a binder phase including an optionally substituted phenolic resin;
 - (ii) synthetic mesophase carbon from aromatic hydrocarbons and;
 - (iii) inorganic filler particles suitable for use as refractory material for high temperature applications.
2. A composition is claimed in claim 1 wherein the phenolic resin is a phenol-
10 aldehyde type resin.
3. A composition is claimed in claim 2 wherein the phenol-aldehyde type resin is a phenol-formaldehyde type resin.
4. A composition as claimed in any one of claims 1 to 3 wherein the phenolic resin is selected from either resole or novolac and phenolic imide or phenolic
15 polyamide or mixtures thereof.
5. A composition as claimed in any one of claims 1 to 4 wherein the phenolic resin is substituted with alkyl or imide.
6. A composition as claimed in claim 5 wherein the alkyl is methyl or t-butyl.
7. A composition as claimed in claim 5 wherein the imide is maleimide or
20 succinimide.
8. A composition as claimed in any one of claims 1 to 7 where the refractory material is one or more of non oxide refractory materials.
9. A composition as claimed in claim 8 wherein the non oxide refractory material is boride, carbide and/or nitride.
- 25 10. A composition as claimed in claim 9 wherein the boride is titanium diboride and/or zirconium diboride.
11. A composition as claimed in claim 9 wherein the carbide is silicon carbide or titanium carbide.
12. A composition as claimed in claim 9 wherein the nitride is silicon nitride or
30 aluminium nitride.

13. A composition as claimed in any one of claims 1 to 12 further comprising an additive selected from the group consisting of crosslinkers, polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and/or sources of formaldehyde.
- 5 14. A composition as claimed in claim 13 wherein the crosslinker is hexamine (hexamethylene tetramine (HMTA)).
15. A composition as claimed in claim 13 wherein the source of formaldehyde is formalin, paraform or trioxane.
16. A composition as defined in any one of claims 1 to 15 wherein the binder
10 phase is selected from the group consisting of novolac-HMTA, novolac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resol-carbon-novolac-HMTA-FA, novolac-HMTA-FA carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂ resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA or polyimide-novolac.
- 15 17. A composition as defined in claim 16 wherein the binder phase is novolac-FA-HMTA.
18. A composition as claimed in any one of claims 1 to 17 wherein the mesophase carbon is in the form of fibres, pellets, platelets or powder.
19. A composition as claimed in any one of claims 1 to 18 wherein the
20 mesophase carbon is 100% anisotropic mesophase derived from naphthalene.
20. A composition as claimed in any one of claims 1 to 18 wherein the mesophase carbon is pre-treated by heating.
21. A composition as claimed in any one of claims 1 to 19 wherein the polymer or polymer composite and/or mesophase carbon are presented in the form of a
25 solution.
22. A composition as claimed in claim 21 wherein the solvent used in the solution is inert or chemically reactive.
23. A composition as claimed in claim 22 wherein the solvent is incorporated in the polymer or polymer composite.
- 30 24. A composition as claimed in claim 22 or claim 23 wherein the solvent is water or an organic solvent.

25. A composition as claimed in claim 24 wherein the organic solvent is an aromatic, ketone, alcohol, ester, ether or mixtures thereof.
26. A composition as claimed in any one of claims 1 to 25 wherein other additives known in the polymer art are included in the polymer, polymer composite and/or synthetic mesophase carbon mixture.
27. A composition as claimed in any one of claims 21 to 26 wherein the mesophase carbon is combined with a solution of novolac/HMTA/FA.
28. A method for preparing a carbon-containing material including the steps of:
- (a) mixing a binder phase containing an organic resin component or polymer composite with synthetic mesophase carbon and inorganic filler particles suitable for use as refractory material for high temperature applications;
 - (b) curing the mixture; and
 - (c) carbonising the cured mixture to above 800°C.
29. A method as claimed in claim 28 wherein the mixture of the binder phase and the mesophase carbon is cured at temperatures up to about 205°C under pressure.
30. A method as claimed in claim 28 or 29 wherein the cured mixture is heated up to temperatures above about 800°C.
31. A method as claimed in claim 30 wherein the temperature is about 1000°C.
32. An article which is wholly or partly manufactured from the carbon-containing material defined in any one of claims 1 to 32.
33. An article as claimed in claim 32 which is steel fabrication equipment or other engineering products.
34. An article as claimed in claim 33 wherein the steel fabrication equipment is slide gates or valves, tap hole blockers or blast furnace linings.
35. An article as claimed in claim 34 which is used as part of an electrode in the electrolytic production of metals.
36. An article as claimed in claim 35 wherein the metals are aluminium and/or magnesium.
37. An article as claimed in claim 32 or 36 which is used as a refractory liner in furnaces used for high temperature processing of materials.

38. An article as claimed in claim 37 wherein the materials are ferrous and non ferrous metals, glasses and ceramics.

39. An article as claimed in claim 33 wherein the engineering product is thermal protection barriers, aerospace components or aircraft, satellite or space craft structures.

5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00236**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. ⁷: C08K 3/04; C04B 35/52, 35/524

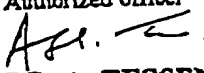
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
C08K 3/04; C04B 35/52, 35/524Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC AS ABOVEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT : WPAT, JAPIO**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10-324812 A (KAWASAKI STEEL CORP) 8 December 1998. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39,41-46,48
X	JP 10-158064 A (KYOCERA CORP) 16 June 1998. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39,41-46,48
X	JP 07-315931 A (NIPPON CARBON CO LTD) 5 December 1995. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39,41-46,48

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

- * Special categories of cited documents:
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Date of the actual completion of the international search
12 April 2000Date of mailing of the international search report
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PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. (02) 6285 3929Authorized officer

DR. A. TESSEMA
Telephone No : (02) 6283 2271

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00236

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member		
US	4983451	FR	2619104	US	5071700	JP 1-133914
						END OF ANNEX

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00236

DOCUMENTS CONSIDERED TO BE RELEVANT		
C (Continuation).		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 91-284638, Class A60, JP 3-187908 A (NIPPON CARBON KK) 15 August 1991 abstract	1-19,29,39, 41-46,48
X	Derwent Abstract Accession No. 88-317782, Class A35, JP 63-233074A (SUMITOMO METAL IND KK) 28 September 1988 abstract	1-19,29,39, 41-46,48
X	JP 9-132461 A (NKK CORP; ADO KEMUKO KK) 20 May 1997. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39, 41-46,50,51
X	Derwent Abstract Accession No. 92-180180, Class Q11, JP 4-117439 A (BRID) 17 April 1992 abstract	1-19,29,39, 41-46,47
X	Derwent Abstract Accession No. 93-172771, Class Q63, JP 5-105869 A (TTUN) 27 April 1993 abstract	1-19,29,39, 41-41,47
X	US 4983451 A (SUGINO et al.) 8 January 1991 col. 1, lines 13-15; col. 4, lines 33-59; col. 5, line 63-col. 6, line 17; claims 1, 2, 8	1-24,26,29- 39,41-46,52
X	EP 466962 A (SIGRI GMBH) 22 January 1992 whole document	1-19,29-39, 41-46,52
X	EP 818510 A (AMOCO CORPORATION) 14 January 1998 col. 1, line 23-col. 2, line 53; col. 3, line 14-col. 4, line 13; claims 1-6, 8, 9	1-19,29-39, 41-46,50,51
P,X	WO 9965843 A (ALLIEDSIGNAL INC.) 23 December 1999 page 2. Line 13-page 3, line 25; page 4, lines 10-33	1-19,29-39, 41-46,52

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NOTIFICATION OF THE RECORDING
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101 Collins Street
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AUSTRALIE

Date of mailing (day/month/year) 13 June 2000 (13.06.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference #27016dab:ct	
International application No. PCT/AU00/00236	International filing date (day/month/year) 23 March 2000 (23.03.00)

1. The following indications appeared on record concerning:	
<input type="checkbox"/> the applicant	<input type="checkbox"/> the inventor <input checked="" type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address CARTER SMITH & BEADLE Qantas House 2 Railway Parade P.O. Box 557 Camberwell, Victoria 3124 Australia	State of Nationality
	State of Residence
	Telephone No. 03 9882 0599
	Facsimile No. 03 9882 9854
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Name and Address FREEHILLS CARTER SMITH & BEADLE 101 Collins Street Melbourne, VIC 3000 Australia	State of Nationality
	State of Residence
	Telephone No. 61 3 9288 1577
	Facsimile No. 61 3 9288 1567
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Date of mailing (day/month/year) 23 October 2000 (23.10.00)	
International application No. PCT/AU00/00236	Applicant's or agent's file reference #27016dab:ct
International filing date (day/month/year) 23 March 2000 (23.03.00)	Priority date (day/month/year) 23 March 1999 (23.03.99)
Applicant QIAO, Greg, GuangHua et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

04 October 2000 (04.10.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08K 3/04, C04B 35/52, 35/524	A1	(11) International Publication Number: WO 00/56811 (43) International Publication Date: 28 September 2000 (28.09.00)
(21) International Application Number: PCT/AU00/00236 (22) International Filing Date: 23 March 2000 (23.03.00) (30) Priority Data: PP 9413 23 March 1999 (23.03.99) AU (71) Applicant (for all designated States except US): THE UNIVERSITY OF MELBOURNE [AU/AU]; Grattan Street, Parkville, VIC 3052 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): QIAO, Greg, GuangHua [AU/AU]; 2/44 Passifeld Street, Brunswick, VIC 3055 (AU). SOLOMON, David, Henry [AU/AU]; 95 Watson Road, Officer, VIC 3809 (AU). SHAW, Raymond, Walter [AU/AU]; 118 Kirribilli Road, New Gisborne, VIC 3438 (AU). JURIC, Drago, Dragutin [AU/AU]; 6 Ben Nevis Court, Bulleen, VIC 3105 (AU). (74) Agent: FREEHILLS CARTER SMITH & BEADLE; 101 Collins Street, Melbourne, VIC 3000 (AU).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: IMPROVED CARBON-CONTAINING MATERIALS (57) Abstract The invention relates to a composition suitable for the preparation of a carbon-containing material including: (i) a binder phase containing organic resin component or polymer composite; (ii) mesophase carbon; and (iii) optionally filler particles. The invention further relates to a method for preparing a carbon-containing material including the steps of: (a) mixing a binder phase containing an organic resin component or polymer composite with mesophase carbon and optionally filler particles; (b) curing the mixture; and (c) heating the cured mixture. The invention also provides an article which is wholly or partly manufactured from the carbon-containing material defined above.		

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IMPROVED CARBON-CONTAINING MATERIALS

The invention relates to improved carbon-containing materials, methods for their preparation and articles manufactured from them, in particular steel fabrication equipment, electrodes in electrolytic cells used in aluminium production, refractories in high temperature furnaces and other engineering products.

Carbon bonded composite materials are finding increasing use as replacements for traditional ceramic composites. Such replacement usually results in greatly improved properties and processing ability. Examples can be found in a wide range of industries which include those manufacturing refractory products such as steel fabrication equipment and electrolytic cells used in aluminium production.

In the preparation of carbon bonded composites, an organic polymer phase is converted to a type of carbon during heating which usually progresses through various temperatures of up to 2000°C. These composites also generally contain carbon black fillers which are added to control rheological properties, assist in processing or improve mechanical properties. The physical state of the carbon may vary from fine particles to fibers and platelets.

Although this practice has been adopted for many years, the effect of carbon black on the organic polymer phase formation during curing and the carbon structure produced during pyrolysis has received little or no attention. We have now found that carbon black has a significant impact on the final formation of the carbon material from the polymer. In general, the porosity of the carbon material derived from polymer resin will increase when more carbon black is added. This porous structure results in low density and sub optimum mechanical properties. We have also found that other carbon sources such as pulverized graphite or carbon derived from pyrolysis of phenolic resins exhibit similar effects to carbon black.

Mesophase carbon was developed in the last few years for the purpose of making graphitic carbon at relative low temperatures of 2000 to 2500°C. Mesophase carbon may be derived synthetically or from petroleum pitch.

Synthetic mesophase which can be derived from aromatic hydrocarbons such as naphthalene consists of up to 100% anisotropy, while mesophase derived from petroleum pitch usually has up to 75% anisotropy. Synthetic mesophase was developed as a superior precursor to graphitisation and is extensively used in carbon fiber applications. Such materials are usually used as a binderless mould and application temperatures are generally more than 2000°C.

We have now found that when mesophase carbon is used as a filler in combination with an organic polymer binder that carbon materials having unexpected and improved properties are obtained. These carbon materials generally have a low porosity measured as a low surface area, high carbon yield, high composite density and good mechanical properties.

According to one aspect of the present invention there is provided a composition suitable for the preparation of a carbon-containing material including:

- (i) a binder phase containing an organic resin component or a polymer composite;
- (ii) mesophase carbon; and
- (iii) optionally filler particles.

According to another aspect of the present invention there is provided a method for preparing a carbon-containing material including the steps of:

- (a) mixing a binder phase containing an organic resin component or polymer composite with mesophase carbon and optionally filler particles;
- (b) curing the mixture; and
- (c) heating the cured mixture.

The term "organic resin component" is used herein in its broadest sense to denote low molecular weight polymerisable entities through to higher molecular weight entities containing many repeat units. The term includes monomers, dimers and oligomers.

A wide range of resin structures are possible but generally this structure will be dictated by resins with a low number of heteroatoms and high carbon content. Suitable resins are those of the formulae (I) and (II) respectively:

R - XH (I)

POLYMER - R - XH (II)

wherein X is oxygen, sulphur or nitrogen and R is aryl, imidoaryl, alkyl, alkenyl,
5 alkynyl or heterocyclyl which may be optionally substituted.

In this specification "optionally substituted" means a group that may or
may not be further substituted with one or more groups selected from alkyl,
alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy,
alkoxy, alkenyloxy, alkynyloxy, aryloxy, carboxy, benzyloxy haloalkoxy,
10 haloalkenyloxy, haloalkynyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl,
nitroalkynyl, nitroaryl, nitroheterocyclyl, azido, amino, alkylamino, alkenylamino,
alkynylamino, arylamino, benzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl,
acylamino, acyloxy, aldehydo, alkylsulphonyl, arylsulphonyl,
alkylsulphonylamino, arylsulphonylamino, alkylsulphonyloxy, arylsulphonyloxy,
15 heterocyclyl, heterocycloxy, heterocyclylamino, haloheterocyclyl, alkylsulphenyl,
arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, arylthio, acylthio
and the like.

Organic resins components having hydroxyl groups such as those of the
formulae (I) and (II) above wherein X is oxygen and R is optionally substituted
20 aryl, for example, phenolic resins or substituted phenolic resins are preferred.
Suitable phenolic resins include phenol-aldehyde type resins such as
phenol-formaldehyde type resins, for example, resole or novolac and phenolic
imide or phenolic polyimide. It will be appreciated that the phenolic resins may
be substituted with any non-deleterious substituent including alkyl, for example,
25 methyl or t-butyl; or imide, for example, maleimide or succinimide.

The desirable composite will have a heteroatom, such as nitrogen in the
system from polymer or crosslinker or solvent. This can be done by using an
organic binder having nitrogen, such as polymide; crosslinker, such as HMTA; or
a solvent, such as pyridine.

30 The term "polymer composite" is used herein in its broadest sense and
refers to the combination of an organic resin component with another material,

such as, for example, other polymers, particulate matter and/or additives known in the polymer art. It will be appreciated that one or more of the other materials may be inert or chemically reactive. The polymers may be selected from those defined above and can be in the form of a solution, dispersions, fibers or particles. The additives may include crosslinkers such as hexamine which is also known as hexamethylene tetramine (HMTA), polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and sources of formaldehyde such as formalin, paraform or trioxane. Suitable polymer composites include novolac-HMTA, novolac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resole-carbon-novolac-HMTA-FA, novolac-HMTA-FA-carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂-resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA and polyimide-novolac. A preferred polymer composite is novolac-FA-HMTA.

The mesophase carbon can be in the form of fibers, pellets, platelets or powder. The powder form can be obtained by pulverising the mesophase in a ball mill. As discussed above, the mesophase may be derived synthetically from aromatic hydrocarbons such as naphthalene or from petroleum pitch. Examples include 100% anisotropic mesophase derived from naphthalene and 75% anisotropic mesophase derived from petroleum pitch. The 100% anisotropic naphthalene may be prepared by cationic oligomerisation catalysed by HF/BF₃. The mesophase may be untreated or pre-treated by heating generally up to about 600°C.

The selection of filler particles largely depends upon the intended use of the carbon containing material. Examples of particulate matter include coated or uncoated fibers, platelets, pigments, fillers, polyesters, metallic mesh, silicon oxides, graphite, carbon black, carbides or nitrides and inorganic material such as aluminium, magnesia, zirconia, bauxite, clay, alumina, titanium diboride, zirconium diboride or titanium oxide. For instance, the inclusion of titanium diboride fillers provides a carbon material which can be used as a wetted cathode in advanced aluminium reduction cells.

The organic resin component, polymer composite and/or mesophase carbon may be presented in the form of a slurry, suspension or dispersion. The solvent used in the slurry, suspension or dispersion can be inert or chemically reactive and may contribute to the properties of the organic resin component or polymer composite. It is often advantageous for the solvent or its reaction products to be incorporated into the polymer derived carbon. This also reduces the loss of weight of the organic resin component or polymer composite on curing. The choice of solvent will depend on the type of organic resin component, polymer composite and/or mesophase carbon employed. An example of such a solvent is furfuryl alcohol. Other solvents include water or organic solvents such as aromatics, for example, toluene or benzene; ketones, for example, methyl ethyl ketone; alcohols, for example, FA or glycol (G); esters; ethers, for example, tetrahydrofuran (THF) or dioxane; or mixtures thereof.

Other additives known in the polymer art such as those defined above may also be included in the organic resin component, polymer composite and/or mesophase carbon mixture. In a preferred embodiment, the mesophase carbon is combined with a solution of novolac/HMTA/FA.

The binder phase may be mixed with the mesophase carbon in step (a) of the method of the invention using any suitable known apparatus, such as, for example, an Eirich mixer. The mixture of the binder phase and the mesophase carbon is generally cured at temperatures up to about 205°C. Curing is normally carried out under atmospheric pressure but can employ vacuum assistance or use elevated pressure in autoclaves to either draw off or retain more volatile species in specific mixtures. The cured mixture is then heated or pyrolysed in step (c) at temperatures sufficient to carbonise the material to a suitable form. This occurs at temperatures above about 800°C but higher temperatures may be employed to further improve the structure and chemical stability. In certain applications, the final temperature can be as high as about 2000°C. The choice of temperature in part depends on the composition and properties of any filler particles, and on the desired end use.

The carbon-containing material of the present invention has many desirable properties including controlled surface area, high density, good mechanical strength, Strain to Failure (StF) values and anti-corrosion properties. For example, the carbon-containing material may have a total surface area of 20 m²/g (Langmuir method) which gives excellent anti-corrosion, a high mechanical strength of about 60 MPa after curing and about 58 MPa after heating, a high carbon density of more than about 1.4 g/cm³ and improved oxidation resistance with the oxidation temperature under O₂ being higher than about 570°C.

These desirable properties enable the carbon-containing material of the present invention to have various industrial applications. High performance carbon materials having anti-corrosion properties are often required by the refractory industry to form cathodes in aluminium reduction cells or bricks in steel making vessels. On the other hand, good mechanical and anti-oxidation properties of carbon materials are important in the products used in steel processing.

Thus, the present invention also extends to articles manufactured from the carbon-containing material, for example, steel fabrication equipment such as slide gates or valves, tap hole blockers and blast furnace linings, electrolytic cells used in aluminium production and other engineering products such as thermal protection barriers, aerospace components and aircraft, satellite and space craft structures.

The method used to prepare the carbon-containing material of the present invention is simple and the precursors of the binder phase and the mesophase carbon are commercially available and cheap. Accordingly, the present invention has the capability of producing a high performance material in an efficient and economical way.

The invention will now be described with reference to the following examples. These examples are not to be construed as limiting the invention in any way.

In the examples, reference will be made to the accompanying drawings in which:

Figure 1 is a graph showing a comparison between the surface areas of carbon materials containing mesophase and carbon black;

Figure 2 is a graph showing a comparison between the densities of carbon materials containing mesophase and carbon black;

5 Figure 3 is two graphs showing a comparison between the maximum strength of carbon materials containing mesophase and carbon black after (a) curing and (b) heating;

Figure 4 is six scanning electron microscope (SEM) images of composites having resin and (a)-(c) carbon black and (d)-(f) mesophase;

10 Figure 5 is three graphs showing (a) pore size distribution of carbon made from 100% polymer after pyrolysis to 1000°C, (b) pore size distribution of carbon made from 50% CB in polymer after pyrolysis to 1000°C and (c) pore size distribution of carbon made from 50% MPN in polymer after pyrolysis to 1000°C; and

15 Figure 6 is a graph comparing carbon densities from composites made using an additive of carbon black (CB) and mesophase (MPN) in a material containing titanium diboride filler particles.

EXAMPLE 1

20 A mesophase pitch synthesised from naphthalene by catalytic reduction with HF/BF_3 is pre-heated under constant argon flow (7 ml/min). The pre-heating program used was 50°C/h to 500°C, keeping at that temperature for 1 hour followed by further 50°C/h to 600°C. The pre-treated mesophase was then pulverised with a ball mill for 1 min into powder before being blended with
25 novolac resin with HMTA as the crosslinker in the solvent FA. The ratio of novolac/HMTA/FA was 40/8/52. Various samples with different ratios of resin and mesophase were prepared using this method and subsequently cured to 205°C over approximately 30 hrs at atmospheric pressure.

30 The cured composites were then pyrolysed to 1000°C at a rate of 50°C/h under an argon flow at 7 ml/min. The carbon-containing material produced was subsequently pulverised into a grain before various property tests were conducted.

Figure 1 shows the surface area of these carbon samples compared with samples prepared using the same methods, but where the mesophase was replaced by carbon black (CB). The surface area was obtained by measuring with N₂ at 77 K using a Langmuir Equation. The results show that, unlike the carbon black as a filler, the mesophase/resin system produces a low porosity carbon-containing material.

EXAMPLE 2

The pre-treated mesophase obtained in Example 1 was mixed with a novolac/HMTA (40/8 in ratio) resin powder in various amounts. 1 g of each mixed sample was then cold moulded into a block having the dimensions of 13 mm in diameter and 5-6 mm in thickness. The pressure used in moulding was 400 kg/cm². The blocks were then cured and carbonised as described in Example 1. The bulk densities of the blocks after moulding, curing and carbonisation were calculated by measuring their dimension and weight.

Figure 2 shows that final carbon densities are higher with resins blended with mesophase compared to those blended with carbon black produced in the same way. Such high density results in a high strength in the mechanical tests as shown in Figures 3a and 3b. After curing, the maximum strength of the blocks were similar in the range of additive to about 70 to 90% with both mesophase and carbon black derived blocks. However, pyrolysed blocks in the same range have a much higher maximum strain when mesophase is blended with the resin. The carbon black blended carbon material has a poor mechanical strength after pyrolysis.

The surface area measurement of the samples pulverised from the blocks resulted in the similar effects observed in Example 1.

EXAMPLE 3

The effects of carbon material derived from other sources, but not mesophase were also tested with a novolac resin. The novolac/HMTA/FA system described in Example 1 was blended with 50% of carbon powder pulverised from

other carbon sources. These carbon sources include pulverised graphite, carbon obtained from the pyrolysis of pure novolac/HMTA/FA to 1000°C and carbon of the same pure resin after pre-treatment using the profile described in Example 1. The resulting mixtures were then cured and pyrolysed to 1000°C as described in

5 Example 1. Table 1 shows that these carbon sources have similar effects to carbon black on the porosity of the final formed carbon/carbon composite.

Different types of mesophase were tested under the same conditions and the results are shown in Table 1 below. The other mesophase carbons used were mesophase derived from naphthalene without pre-treatment and mesophase

10 derived from pitch with about 75% anisotropy. Table 1 indicates that these mesophase carbons have a similar effect on the porosity of the final formed carbon materials as pre-treated mesophase. The pyrolysis weight loss is also much higher.

15 **Table 1.** Effect of other carbon fillers on the carbon material formation from a novolac/HMTA/FA mixed system

	50% Carbon Black	50% pre-treated mesophase	50% graphite	50% resin carbon	50% pre- treated resin	50% un-treated mesophase	50% pitch mesophase
Cure Weight Loss (%)	11	12	10	19	12	11	13
Pyrolysis Weight Loss (%)	18	25	19	25	21	35	27
Surface Area (m ² /g)	266	33	46	266	215	12	17

EXAMPLE 4

The novolac/HMTA/FA system described in Example 1 was blended with 50% carbon black or 50% treated mesophase powder pulverized by a ball mill method. The composites formed with this method were then cured and pyrolysed to 1000°C as described in Example 1 being subjected to scanning electron microscopy (SEM) as shown in Figure 4. Figures 4a to 4c are the SEM images of the composite having 50% carbon black resin with different amplification. Figures 4d to 4f are the equivalent images of the composite having 50% mesophase and resin. As shown in the figures, the images with resin/carbon black composites appears as a non-homogeneous form where the carbon black powder can be clearly identified. On the other hand, the image of the block from the resin/mesophase composite gives a uniform material, indicating a strong interaction between resin and mesophase during curing and pyrolysis.

EXAMPLE 5

The novolac/HMTA/FA system described in Example 1 was blended with the powder of 50% carbon black (CB) or 50% mesophase (MPN), respectively. These powders were made by pulverization within a ball mill. The formed composites, together with pure resin, were cured and pyrolysed to 1000°C as described in Example 1. The resultant carbon and carbon composites were degassed under an argon flow at 400°C for 48 hours followed by full isotherm adsorption measurements with nitrogen at 77 K using a ASAP 2010 surface analyzer. A DFT plus software supplied with the analyzer then calculated the measured full isotherm curves to provide the pore size distributions. Figure 5 shows the pore size distributions calculated from these tested samples.

The carbons derived from pure resin polymer gave a low surface area of 21 m²/g and no significant micropores appeared in the distribution, as shown in Figure 5(a). However, when 50% carbon black was mixed with the resin, the measured surface area increased to 266 m²/g as shown in Table 1 above and this porosity is mainly contributed by micropores (8-10 Å pore width, Figure 5(b)). Assuming that the low surface area carbon black (~10 m²/g) did not become

porous during the pyrolysis based on the results in Figure 1, the huge porosity from the composites with CB was obviously due to the effect of adding carbon black to the resin polymer during its carbonization. When 50% MPN was used, this additive did not create any significant micropores in the carbons derived from polymer (Figure 5(c)). Therefore, using MPN to replace CB as an additive in the composite avoids the formation of micropores in carbon derived from polymer.

EXAMPLE 6

Two types of cement were formed by mixing of 24% of novolac, 34% of furfuryl alcohol, 4.6% of HMTA and 37.4% of two different additives: carbon black and mesophase, respectively. 6.5% of each of these two cements was then mixed, respectively, with 93.5% titanium diboride (TiB_2). Two batches of 5.1 kg of each mixture were then compacted in a vibroformer make a lab block of the size about 150 x 150 x 60 mm. The pressure used to compact the block was standard pressure of 200 psi x 50 followed by vibration forming at ~ 100 psi. The densities of the formed lab blocks and their saturation values are given in Table 2 below.

Table 2. Physical data of tested lab blocks after compaction and pyrolysis

Sample Name	CB1	CB2	MPN1	MPN2
Density after compaction (g/cm^3)	3.45	3.54	3.52	3.52
Saturation after compaction (%)	90.0	92.4	91.8	91.8
Shrinkage after pyrolysis (%)	0.03	-0.19	-0.35	-0.31
Weight Loss after pyrolysis (%)	1.95	1.95	2.27	2.30

These blocks were then cured to 205 °C in an oven, and pyrolysed to 1000 °C while the blocks were packed in petroleum coke. The total weight losses after pyrolysis were similar for both types of composites and there was no obvious size shrinkage observed from these blocks (Table 2). However, the

density of the carbon composite made with MPN as an additive has a value of 3.44 g/cm^3 compared with the value of 3.38 g/cm^3 of the composite using carbon block as an additive (Figure 6).

5 EXAMPLE 7

Each of the 4 lab blocks of the carbon composites obtained in Example 6 was cut in half and then sectioned into 6 strength bars having a size of $25 \times 30 \times 150 \text{ mm}$. These bars were then subjected to a three points bend test. Table 3 below gives the results from these mechanical tests.

10

Table 3. Mechanical test results from 3 points bend test for the composites made using CB and MPN as additives

Samples	CB	MPN
Strength (MPa) (average of 8 bars from the center of the composite)	2.71	6.57
Young's Modulus (MPa) (average of 8 bars)	715	1630
Strain to Failure (StF) (%)	0.38	0.40

The results show that the composites made using MPN as an additive
15 have approximately double the mechanical strength of the composites using CB as an additive. This result is in agreement with the result of the composites formed by polymer/additive only system (Example 2). The Young's Modulus of MPN sample also increased from 715 to 1630 MPa compared to the CB sample. Although the Young's Modulus has increased, the Strain to Failure of
20 MPN sample has also increased from 0.38 % to 0.4 % highlighting the improved mechanical properties.

EXAMPLE 8

The lab blocks of carbon composites obtained in Example 6 were cut into
25 the standard size of $25 \times 30 \times 150 \text{ mm}$ and then subjected to compression tests. Table 4 below shows the results of these tests.

Table 4. Mechanical test results from compression test for the composites made using CB and MPN as additives

Samples	CB	MPN
Strength (MPa) (average of 6 samples)	11.9	25.8
Young's Modulus (MPa) (average of 6 samples)	1057	1720

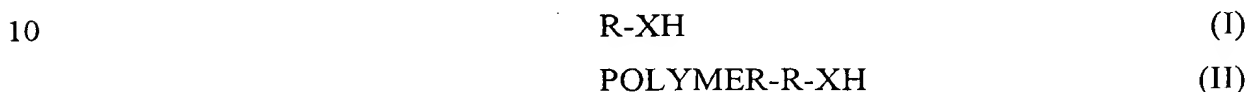
- 5 Similar to the observation in Example 7, the mechanical strength of the MPN sample is 2.5 times stronger than the sample of CB. The Young's Modulus also increased from 1057 to 1720 MPa.

Claims

1. A composition suitable for the preparation of a carbon-containing material including:

- (i) a binder phase containing an organic resin component or polymer composite;
5 (ii) mesophase carbon; and
(iii) optionally filler particles.

2. A composition as claimed claim 1 wherein the organic resin component has the formula (I) or (II):



wherein X is oxygen, sulphur or nitrogen and R is optionally substituted aryl, optionally substituted imidoaryl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl or optionally substituted heterocyclcyl.
15

3. A composition as claimed in claim 2 wherein the organic resin component is of the formula (I) or (II) wherein X is oxygen and R is optionally substituted aryl.

4. A composition as claimed in claim 2 or 3 wherein the organic resin component is an optionally substituted phenolic resin.
20

5. A composition is claimed in claim 4 wherein the phenolic resin is a phenol-aldehyde type resin.

6. A composition is claimed in claim 5 wherein the phenol-aldehyde type resin is a phenol-formaldehyde type resin.

7. A composition as claimed in any one of claims 4 to 6 wherein the phenolic resin is selected from either resole or novolac and phenolic imide or phenolic polyimide or mixtures thereof.
25

8. A composition as claimed in any one of claims 4 to 7 wherein the phenolic resin is substituted with alkyl or imide.

9. A composition as claimed in claim 8 wherein the alkyl is methyl or t-butyl.
30

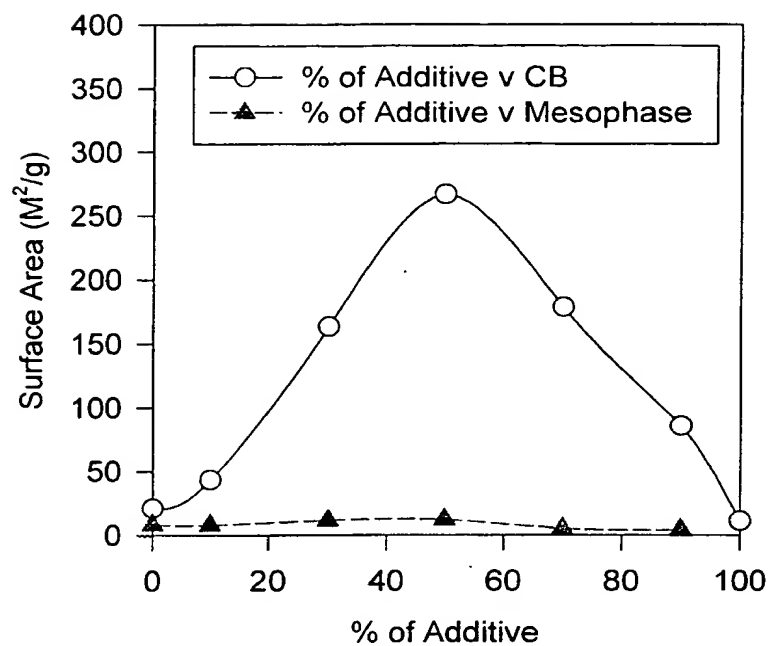
10. A composition as claimed in claim 8 wherein the imide is maleimide or succinimide .
11. A composition as claimed in any one of claims 1 to 10 wherein the polymer composite is a combination of an organic resin component with another
5 material.
12. A composition as claimed in claim 11 wherein the material is other polymers, particulate matter and/or additives known in the polymer art.
13. A composition as claimed in claim 11 or 12 wherein the polymer is an organic resin component as defined in any one of claims 2 to 10.
- 10 14. A composition as claimed in any one of claims 11 to 13 wherein the polymer is in the form of dispersions, fibers or particles.
15. A composition as claimed in any one of claims 14 to 16 wherein the particulate matter is coated or uncoated fibers, platelets, pigments, fillers, polyesters, metallic mesh, silicon oxides, graphite, carbon black, carbides,
15 nitrides and/or inorganic material.
16. A composition as claimed in claim 15 wherein the inorganic material is a refractory material suitable for high temperature applications.
17. A composition as claimed in claim 15 wherein the inorganic material is an oxide or silicate.
- 20 18. A composition as claimed in claim 17 wherein the oxide or silicate is magnesia, zirconia, chromate, bauxite, clay or alumina.
19. A composition as claimed in claim 16 where the refractory material is one or more of non oxide refractory materials.
20. A composition as claimed in claim 19 wherein the non oxide refractory
25 material is boride, carbide and/or nitride.
21. A composition as claimed in claim 20 wherein the boride is titanium diboride and/or zirconium diboride.
22. A composition as claimed in claim 20 wherein the carbide is silicon carbide or titanium carbide.
- 30 23. A composition as claimed in claim 20 wherein the nitride is silicon nitride or aluminium nitride.

24. A composition as claimed in any one of claims 12 to 23 wherein the additives are crosslinkers, polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and/or sources of formaldehyde.
25. A composition as claimed in claim 24 wherein the crosslinker is
5 hexamine (hexamethylene tetramine (HMTA)).
26. A composition as claimed in claim 24 wherein the source of formaldehyde is formalin, paraform or trioxane.
27. A composition as claimed in any one of claims 11 to 26 wherein the
10 polymer composite is novolac-HMTA, novolac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resol-carbon-novolac-HMTA-FA, novolac-HMTA-FA carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂ resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA or polyimide-novolac.
28. A composition as claimed in any one of claims 11 to 27 wherein the
15 polymer composite is novolac-FA-HMTA.
29. A composition as claimed in any one of claims 1 to 28 wherein the mesophase carbon is in the form of fibers, pellets, platelets or powder.
30. A composition as claimed in any one of claims 1 to 29 wherein the mesophase is derived synthetically from aromatic hydrocarbons.
- 20 31. A composition as claimed in claim 30 wherein the aromatic hydrocarbons are hydrocarbons, naphthalene or petroleum pitch.
32. A composition as claimed in any one of claims 1 to 31 wherein the mesophase carbon is 100% anisotropic mesophase derived from naphthalene or 75% anisotropic mesophase derived from petroleum pitch.
- 25 33. A composition as claimed in any one of claims 1 to 32 wherein the mesophase carbon is pre-treated by heating.
34. A composition as claimed in any one of claims 1 to 33 wherein the polymer or polymer composite and/or mesophase carbon are presented in the form of a solution.
- 30 35. A composition as claimed in claim 34 wherein the solvent used in the solution is inert or chemically reactive.

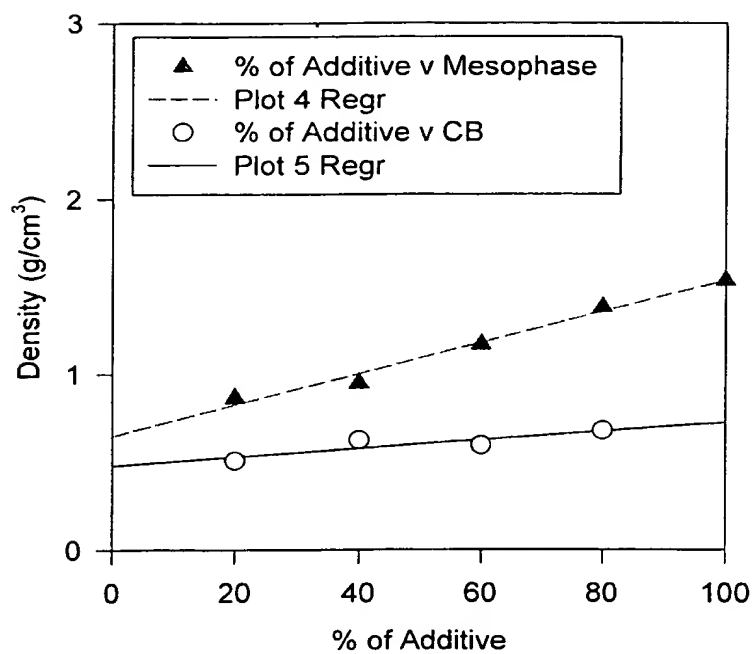
36. A composition as claimed in claim 35 wherein the solvent is incorporated in the polymer or polymer composite.
37. A composite as claimed in claim 35 or claim 36 wherein the solvent is water or an organic solvent.
- 5 38. A composition as claimed in claim 37 wherein the organic solvent is an aromatic, ketone, alcohol, ester, ether or mixtures thereof.
39. A composition as claimed in any one of claims 1 to 38 wherein other additives known in the polymer art are included in the polymer, polymer composite and/or mesophase carbon mixture.
- 10 40. A composition as claimed in any one of claims 34 to 39 wherein the mesophase carbon is combined with a solution of novolac/HMTA/FA.
41. A method for preparing a carbon-containing material including the steps of:
- (a) mixing a binder phase containing an organic resin component or
 - 15 polymer composite with mesophase carbon and optionally filler particles;
 - (b) curing the mixture; and
 - (c) heating the cured mixture.
42. A method as claimed in claim 41 wherein the mixture of the binder phase and the mesophase carbon is cured at temperatures up to about 205°C under
- 20 pressure.
43. A method as claimed in claim 41 or 42 wherein the cured mixture is heated up to temperatures above about 800°C.
44. A method as claimed in claim 43 wherein the temperature is about 1000°C.
- 25 45. An article which is wholly or partly manufactured from the carbon-containing material defined in any one of claims 1 to 40.
46. An article as claimed in claim 45 which is steel fabrication equipment or other engineering products.
47. An article as claimed in claim 46 wherein the steel fabrication equipment
- 30 is slide gates or valves, tap hole blockers or blast furnace linings.

48. An article as claimed in claim 41 or 42 which is used as part of an electrode in the electrolytic production of metals.
49. An article as claimed in claim 48 wherein the metals are aluminium and/or magnesium.
- 5 50. An article as claimed in claim 41 or 42 which is used as a refractory liner in furnaces used for high temperature processing of materials.
51. An article as claimed in claim 50 wherein the materials are ferrous and non ferrous metals, glasses and ceramics.
- 10 52. An article as claimed in claim 46 wherein the engineering product is thermal protection barriers, aerospace components or aircraft, satellite or space craft structures.

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**Figure 1**

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**Figure 2**

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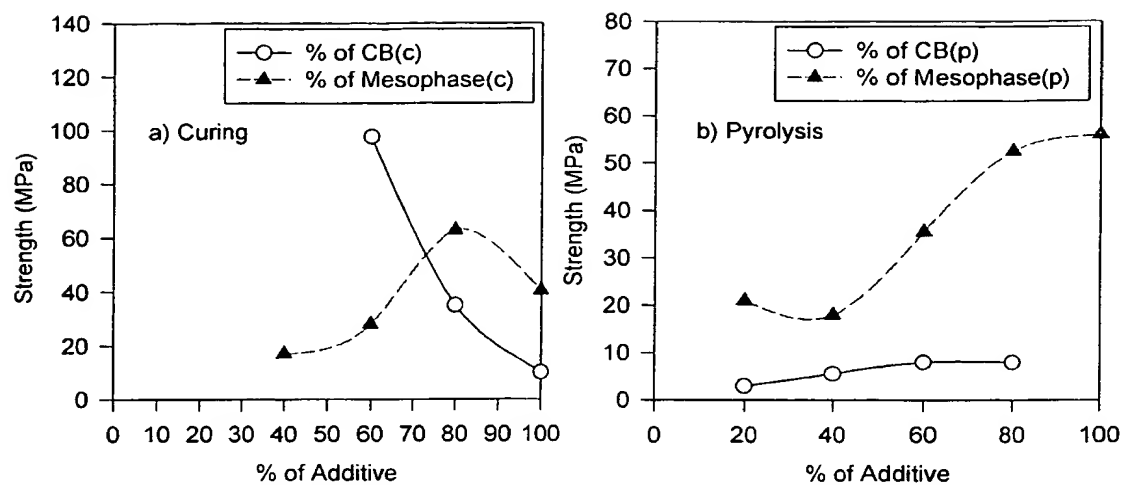
**Figure 3**

Figure 4a



Figure 4d



Figure 4b

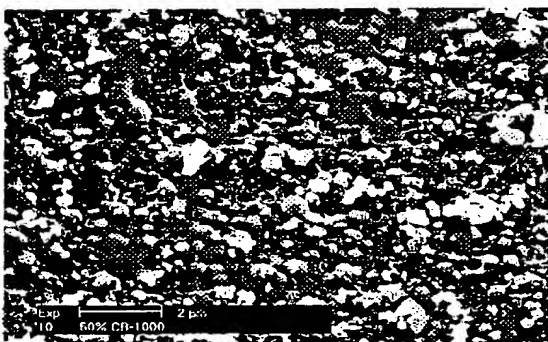


Figure 4e



Figure 4c

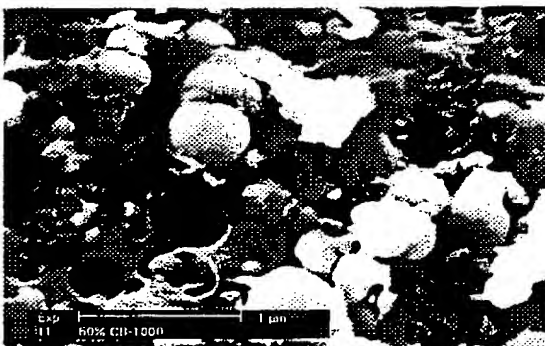
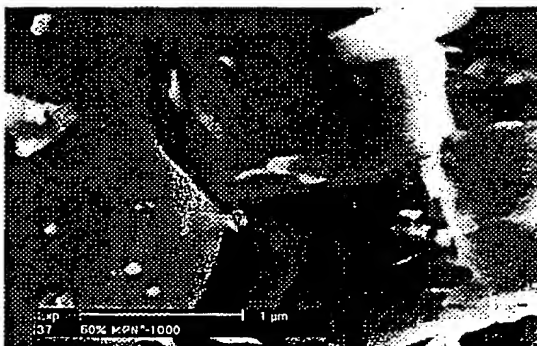


Figure 4f



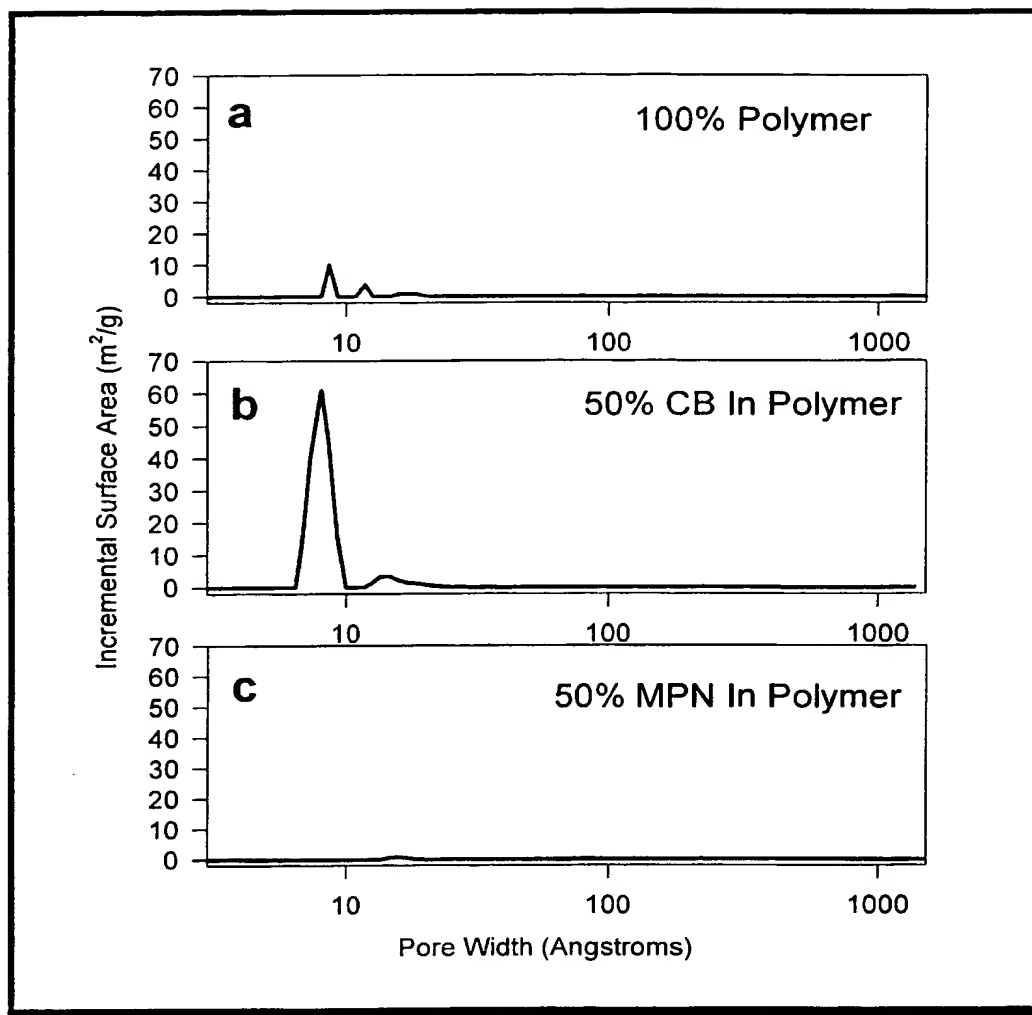
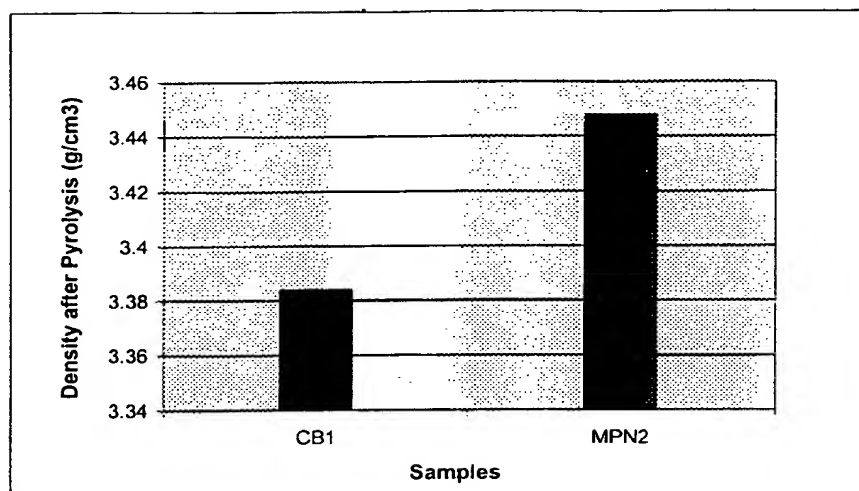


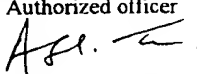
Figure 5

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**Figure 6**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00236

A. CLASSIFICATION OF SUBJECT MATTER																						
Int. Cl. ⁷ : C08K 3/04; C04B 35/52, 35/524																						
According to International Patent Classification (IPC) or to both national classification and IPC																						
B. FIELDS SEARCHED																						
Minimum documentation searched (classification system followed by classification symbols) C08K 3/04; C04B 35/52, 35/524																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC AS ABOVE																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT : WPAT, JAPIO																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
X	JP 10-324812 A (KAWASAKI STEEL CORP) 8 December 1998. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39,41-46,48																				
X	JP 10-158064 A (KYOCERA CORP) 16 June 1998. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39,41-46,48																				
X	JP 07-315931 A (NIPPON CARBON CO LTD) 5 December 1995. In: Patent Abstracts of Japan [CD-ROM]. abstract	1-19,29,39,41-46,48																				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex																						
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E"</td> <td>earlier application or patent but published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L"</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	document published prior to the international filing date but later than the priority date claimed		
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"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family																			
"P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 12 April 2000		Date of mailing of the international search report 19 APR 2000																				
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  DR. A. TESSEMA Telephone No : (02) 6283 2271																				

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00236

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 91-284638, Class A60, JP 3-187908 A (NIPPON CARBON KK) 15 August 1991 abstract	1-19,29,39, 41-46,48
X	Derwent Abstract Accession No. 88-317782, Class A35, JP 63-233074A (SUMITOMO METAL IND KK) 28 September 1988 abstract	1-19,29,39, 41-46,48
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X	EP 466962 A (SIGRI GMBH) 22 January 1992 whole document	1-19,29-39, 41-46,52
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Patent Document Cited in Search Report				Patent Family Member			
US	4983451	FR	2619104	US	5071700	JP	1-133914
							END OF ANNEX